Charge Transport in Non-Diluted Conjugated Polymers

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Abstract

We present a unified calculation method for variable range hopping transport with a varying charge concentration and a varying applied electrical field. We demonstrate that the major differences between the transport properties measured at high concentration and low concentration can be explained within this framework. In particular the difference between the measured mobility, and mobility activation energy in polymer field effect transistors and polymer light emitting diodes is explained. A theoretical method to extract the charge carrier density of state from the transport measurements of non-diluted materials is proposed.

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Charge transport in conjugated polymers is often described in terms of thermal assisted tunneling (hopping) [1, 2] or polaronic transfer mechanism [3] in a disordered array of localized states [4]. As the density of states of the charge carrier has not been directly measured for most of the conjugated polymers, a Gaussian density of states is often assumed. The Gaussian disorder model (GDM) [5] and related models with energetic spatial correlations between the states [6] have been solved previously for non-interacting carriers, or explicitly for low charge density. Such calculations are typically successful in describing the field and temperature dependence of the measured mobility in the steady state regime. The dynamic transport properties at the short time scales, where the charge carriers are far from thermodynamic equilibrium, have been described using different methods [7, 8]. However, all of the mentioned calculations are based on the assumption that the time average occupation of the sites is small and hence, the effect of the charge concentration is negligible.

Two types of experiments demonstrated that the transport depends on the charge density: the super linear increase of current with increasing molecular doping, and the trans-conductance measurements in polymeric field effect transistors (FETs) [9]. Recently, we demonstrated a mobility enhancement in poly-[2-methoxy-5-(2'-ethyl-hexiloxy)-p-phenylenevinylene] (MEH-PPV) FET by a factor of ~ 10 due to charge concentration build up [10] reaching values of up to $3 \cdot 10^{-5}$ cm^2/V sec. In light emitting diodes (LEDs) made from the same polymer the mobility depends strongly on the applied field, with a zero field mobility value of $1 \cdot 10^{-6}$ cm^2/V sec [11] (see also [12]). Typically, FETs operate at much lower electrical fields compared to LEDs and the charge residence time in the device is much longer. Therefore, the increase of the mobility in FETs cannot be explained in terms of electric field dependent mobility or by the dynamical transport behavior at short time scales.

Recently, the mobility [13] and the diffusion coefficient [14] dependence on charge concentration has been calculated using a low field approximation of the GDM, successfully describing the molecular doping effect. Using the energy correlation model with traps, the mobility dependence on electrical field at different charge concentration was calculated [15], resulting in a similar field dependence of the mobility for different carrier densities. In this letter we suggest a unified calculation of the concentration and electrical field dependence, using a semi-classical mean medium approximation (MMA) [16] and demonstrate that the fundamental behavior of the different devices is recovered. Moreover, we

propose a technique to extract the charge carrier density of state.

A specific spatial and energetic configuration of sites is described by its density of states (DOS) and by its spatial distribution function. Here we assume a homogeneous spatial distribution and a Gaussian DOS [17],

$$g\left(\varepsilon\right) = \frac{1}{2\pi\sqrt{\sigma}} \exp\left(-\frac{(\varepsilon - \varepsilon_0)^2}{\sqrt{2\sigma^2}}\right) \tag{1}$$

where σ is defined as the width of the DOS, ε is the energy, and ε_0 is the center of the DOS. We use the Gaussian functional form to enable comparison with other methods. However, we do not expect a change in the principle results discussed here, while replacing the Gaussian DOS with a more accurate (experimentally determined) DOS. The second assumption we use is that the charge transfer process drives the charge carrier population towards equilibrium energy-distribution. To clearly define an equilibrium energy-distribution we assume that each state cannot contain more than one charge carrier (due to columbic repulsion). Therefore the equilibrium distribution function is given by the following Fermi-Dirac form:

$$f\left(\varepsilon, \eta\right) = 1/[1 + \exp\left(\beta\left(\varepsilon_i - \eta\right)\right)] \tag{2}$$

where η is the chemical potential. A transfer rate which will drive the charge carriers toward a detailed equilibrium described in Eq. (2), has the general form of:

$$v_{ij} = v\left(|\varepsilon_j - \varepsilon_i|, \mathbf{R_{ij}}\right) \exp\left[-\frac{\beta}{2}\left[(\varepsilon_j - \varepsilon_i) + |\varepsilon_j - \varepsilon_i|\right]\right] \tag{3}$$

where $\varepsilon_i, \varepsilon_j, \mathbf{R_{ij}}$ are the initial energy, final energy, and the initial-final states vector, respectively; v is an envelope function that depends only on the absolute energy difference and the spatial coordinates, and β is the inverse temperature $(1/kT)$. In the absence of an additional energy dissipation process, and when the form of the transfer rate deviates from Eq. (3) (as in the adiabatic polaronic rate), the charge carriers will never reach thermal equilibrium (Eq. (2)). On the other hand, when the envelope function is decaying exponentially in space, with an inverse localization radii γ $(v = v_0 \exp\left(-\gamma |\mathbf{R_{ij}}|\right))$, the transfer rate becomes the known Miller-Abrahams rate [2], and the charge carriers reach equilibrium after a sufficient time has lapsed.

In order to calculate the transport properties one needs to solve the Master Equation determined by the transfer rate and the energetic and spatial configuration of states, and

to average over all possible configurations. Instead, we propose to use the mean medium approximation (MMA) where averaging on all possible discrete configurations is replaced by solving the transport properties of a homogeneous and continuous media, characterized by the energetic DOS function. Such an approximation is valid only for large enough space and time scales, and where the excess energy gained by the accelerating field is dissipated fast. Under the conditions for which the MMA is valid, one can deduce: 1) the charge carrier population is near detailed equilibrium, and the occupation probability of each site is determined by the local quasi-chemical potential and the equilibrium distribution function. 2) Since the medium is homogeneous all points in space are characterized by the same charge concentration and transfer rates and hence, the relaxation of a charge excess must follow the Poissonian Debye pattern. Namely, the transport has to be Gaussian (Markovian) and can be characterized by the first two spatial moments of the transport Green function which are related to the mobility (μ) and the diffusion coefficient (D). Based on detailed equilibrium and given a DOS and a charge concentration, the Einstein relation (D/μ) can be uniquely derived. As the system is Markovian, one needs only to derive a value for the mobility as a function of charge density and electric field to complete the transport description. We perform this calculation below using the MMA framework.

Before embarking on the mobility calculation we emphasize the importance of charge concentration effects in real devices. We calculated the charge carrier distribution in energy, $p(\varepsilon)$, at equilibrium (Fig. 1) for several chemical potentials (η). As long as the chemical potential is below $\varepsilon_0 - \sigma(\beta\sigma + 2)$ the charge concentration has a Gaussian distribution centered at $\varepsilon_0 - \beta\sigma^2$, and the Boltzmann approximation is valid. For chemical potentials above this value the charge carrier distribution deviates from the Gaussian shape and the average energy increases. At this point the Boltzmann approximation is no longer valid, and one can expect the transport properties of the charge carriers to change. The relevant charge concentration can be then calculated for a given DOS. The total DOS can be estimated as the maximum concentration of electronic units (sites) or one over the molecular volume of such unit (5-10 monomers or 300 atoms volume equivalent to a total DOS of $\sim 10^{20}$ [cm^{-3}]) [18]. For a DOS width of $5kT$ (130 meV at room temperature), and a chemical potential of $\varepsilon_0 - \sigma(\beta\sigma + 2)$, the corresponding charge concentration is approximately 10^{11} [cm^{-3}]. As polymer based electronic devices (as LEDs and FETs) operate at charge concentrations beyond 10^{15} [cm^{-3}], the charge concentration effects should be taken into account. It is evident that for any practical concentration the
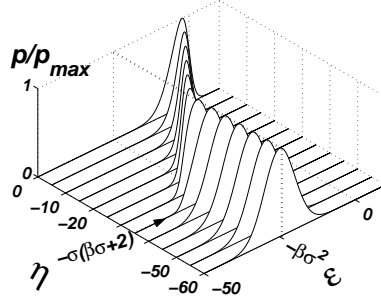
FIG. 1: The normalized charge carrier energetic distribution ($p(\varepsilon)$) at various chemical potentials (η), for a Gaussian DOS ($\sigma = 5/\beta$) centered at energy $\varepsilon=0$. For $\eta > \varepsilon_0 - \sigma(\beta\sigma + 2)$, the energetic charge carrier distribution is modified when compared to the non-degenerate distribution.

charge energy distribution in a Gaussian DOS does not follow the Boltzmann distribution function. Previously we have shown that the D/μ ratio diverges from the classical kT/q value [19]. In the following we will consider the effect of the charge concentration on the mobility.

The total current is calculated by integrating the current between each two sites while applying the MMA assumption that each point contains all possible energy states with a relative weight determined by the DOS function ($g(\varepsilon)$):

$$
\mathbf{J} = \int_{\Re} d\mathbf{R_{ij}} \int_{-\infty}^{\infty} d\varepsilon_i \int_{-\infty}^{\infty} d\varepsilon_j v_{ij}(\mathbf{R_{ij}}, \varepsilon_i, \varepsilon_j) g(\varepsilon_i) f(\varepsilon_i, \eta) g(\varepsilon_j - \mathbf{R_{ij}} \cdot \mathbf{E})
$$
$$
[1 - f(\varepsilon_j - \mathbf{R_{ij}} \cdot \mathbf{E}, \eta)] \mathbf{R_{ij}} \cdot \hat{\mathbf{E}}
\tag{4}
$$

where $\mathbf{R_{ij}} \cdot \hat{\mathbf{E}}$ is the potential drop between sites induced by the electric field E. Inserting the Miller Abrahams hopping rate and selecting the ($|\mathbf{R_{ij}}|, z, \varphi$) coordinate system, where $z = \mathbf{R_{ij}} \cdot \hat{\mathbf{E}}$ and φ is the angle in the plane perpendicular to z, the current integral becomes dependent on one spatial dimension, and reads:

$$
\mathbf{J} = 2\pi \int_{-\infty}^{\infty} dz \int_{-\infty}^{\infty} d\varepsilon_i \int_{-\infty}^{\infty} d\varepsilon_j g(\varepsilon_i) f(\varepsilon_i, \eta) g(\varepsilon_j - (zE)) [1 - f(\varepsilon_j - (zE), \eta)]
$$
$$
\exp\left(-\frac{\beta}{2}((\varepsilon_j - \varepsilon_i) + |\varepsilon_j - \varepsilon_i|)\right) z \exp(-\gamma |z|) (\gamma |z| + 1)
\tag{5}
$$

The mobility is calculated by the definition $\mu \equiv \mathbf{J}/p\mathbf{E}$, where p is the total charge carrier concentration: $p(\eta) = \int g(\varepsilon) f(\varepsilon, \eta) d\varepsilon$. The charge density dependence of the mobility for a range of electrical fields is shown in Fig. 2. We note that the effect of the charge density becomes pronounced for $\eta > \varepsilon_0 - \sigma(\beta\sigma + 2)$ where the system is degenerate, namely non-diluted (see also Fig. 1). At very high charge concentration the mobility

value has a maximum due to "over filling" of the states to the point where there are less states left to transfer into. The figure also shows that at higher electric fields the density dependence is less pronounced and the effect of the DOS form diminishes. At low electric fields, the curve describing the mobility is determined by the shape of the DOS. This can be shown by linearizing Eq. (5) in the limit $\beta |zE| << 1$:

$$\mu_{E \to 0} = \frac{32\pi\beta\upsilon_0}{q\gamma^5 \cdot p(\eta, g(\varepsilon))} \int\limits_{-\infty}^{\infty} d\varepsilon_i \int\limits_{\varepsilon_i}^{\infty} d\varepsilon_j g(\varepsilon_i) f(\varepsilon_i, \eta) g(\varepsilon_j) [1 - f(\varepsilon_j, \eta)] \exp(-\beta(\varepsilon_j - \varepsilon_i))$$

(6)

The low field mobility, given in Eq. (6), depends only on the exact shape of the DOS. Therefore, the DOS shape can be extracted from measurements of the low field mobility dependence on charge concentration, using this equation.

In Fig. 3 the mobility dependence on the electrical field is illustrated, for several charge concentrations. It shows that at the low concentration region all the mobility curves merge to one curve which depends strongly on the field, as expected from the Boltzmann approximation. However, as the charge concentration increases (to a practical value) and the chemical potential crosses the value of $\varepsilon_0 - \beta\sigma(\sigma + 2)$, the low field mobility increases, and the mobility field dependence weakens. At high electrical fields the curves merge again, as the potential drop due to the applied field shifts most of the final sites below that of the initial site ("state saturation"). In any case we expect that the theory used here would not be strictly valid at the extreme cases of high charge concentration and/or high electric fields. For example, it was suggested that at the high field regime the polaron dissociates into a free electron and a structural conformation which is left behind [20], hence a different hopping mechanism should be applied. This can also be viewed as a violation of our assumption that any excess energy gained by the field is dissipated fast enough. The inconsistency between the measured mobility in LEDs and FETs that was pointed out at the beginning of this paper can now be explained using the MMA calculation results. We propose that it steams from the vastly different operating conditions of each device expressed as the typical charge concentration and electric field. The ovals in Fig. 3 denote the typical operation field and concentration ranges in LEDs and FETs. The low concentration, high field condition in LEDs leads to a relatively low, strongly field dependant mobility. On the other hand, in FETs the mobility is typically higher and its dependence on the field is weak, as the gate bias induces a high charge concentration (as was demonstrated in [10]). Similarly, another difference between FETs
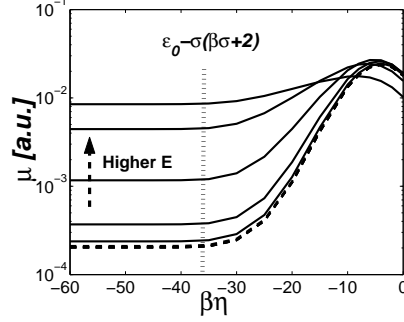
FIG. 2: The mobility versus the chemical potential (for DOS width $\sigma = 5/\beta$). The mobility does not change at the diluted system region ($\eta < \varepsilon_0 - \sigma (\beta\sigma + 2)$), related to charge concentration of $\sim 10^{11}$ [cm^{-3}]).
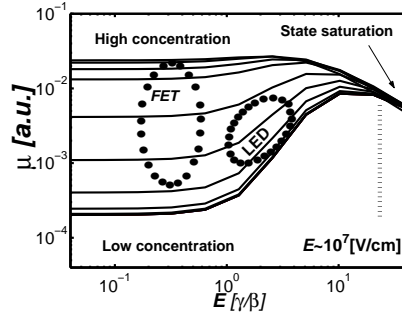

FIG. 3: The mobility versus the electrical field for different charge concentration (for DOS width $\sigma = 5/\beta$). The curves for low charge concentrations ($\eta < \varepsilon_0 - \sigma (\beta\sigma + 2)$) unite. At high charge concentration the mobility remains high and almost independent of the electrical field at most of the electrical field range.

and LEDs is observed while examining the influence of charge carrier concentration on the activation energy of the mobility (Fig. 4). Since the transfer rate of the model is in the Miller-Abrahams form the only possible origin of the activation energy is the energetic disorder (contrary to other possible contribution as the polaronic effect, e.g. Ref. [21]). While the activation energy at high applied fields is low, at low applied fields it is strongly dependent on the charge carrier concentration (insert in Fig. 4). The difference of 200 meV between "low concentration" (LED) mobility activation energy and "high concentration" (FET) activation energy was measured by us (215±10 meV [22] and 400±40 meV [11] in MEH-PPV based FET and LED, respectively) and in Ref. [12]. However, the activation energy measured at high concentrations (FET) is significantly higher than the GDM, Miller-Abrahams model prediction, indicating an additional source
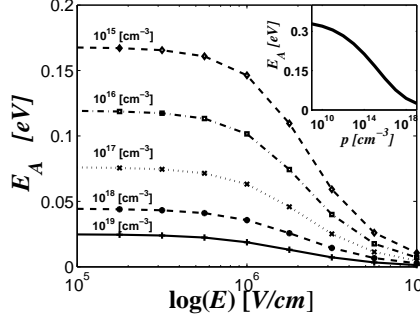
FIG. 4: The activation energy of the mobility versus the electrical field for different charge concentration (for DOS width σ=130 meV, N_V=10^{20} [cm^{-3}] and Miller Abrahams transfer between sites). The activation energy at low electrical field (plotted in the insert) is strongly dependent on the charge concentration and diminishes at high charge concentration.

for the activation energy besides the energetic disorder. Explicitly, the activation energy in the polaronic model is constituted from the energetic disorder contribution and half of the polaronic energy. Therefore, at high concentration measurement, where the energetic disorder contribution is negligible, the polaronic binding energy can be estimated as twice the measured activation energy ($\sim$400 meV for MEH-PPV at the previous example).

In conclusion, we present a unified calculation method for variable range hopping of diluted and non-diluted materials (low and high charge carrier concentration), and a varying applied electric field. We demonstrate that the major differences between the transport properties measured at high concentration (in FETs) and low concentration (in LEDs) can be explained by this model, in particular the difference in the mobility and the activation energy of the mobility between the two. Moreover, the low value of the predicted high concentration activation energy, where compared to measurements, enables us to estimate the polaron binding energy in MEH-PPV as 400$\pm$40 meV. A theoretical method to extract the charge carrier DOS from the charge transport measurements is proposed, as well. Finally, we note that charge concentration effects play a role also in other experimental situations such as time of flight experiments [23].

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